INSTITUTE NOTES.

MAY, 1941.

ANNUAL REVIEWS OF PETROLEUM TECHNOLOGY.

The Council has decided that, in order to effect economies in printing and paper, the *Annual Reviews of Petroleum Technology* will be issued as a special number of the *Journal* to all members and subscribers entitled to receive the ordinary monthly *Journal*. According to present arrangements ten issues only will be made of the *Journal* during 1941. The *Annual Reviews* will be issued in lieu of the August and September issues, about the end of August.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

BEAN, Sidney Herbert, Managing Director, Messrs. Edward Wiggins & Co., Ltd. (*E. R. Redgrove ; E. A. Evans.*)

BROWN, Harry Eugene, Sales Manager, Lobitos Oilfields, Ltd. (*J. S. Parker ; J. Wood-Mallock.*)

CAMERON, William, Refinery Manager, Shell Refining & Marketing Co., Ltd. (*J. A. Oriel ; W. W. Goulston.*)

GIBSON, Arthur Reginald, Technical Representative, Petroleum Board. (*A. E. Hope ; H. E. Priston.*)

HALL, Frederick John Spencer, Chemist, Horton Manufacturing Co., Ltd. (*E. A. Evans ; W. D. Doughty.*)

IVES, Herbert Charles, Chief Chemist, Messrs. W. H. Willcox & Co., Ltd. (*E. E. Manning ; L. O. Maskell.*) (*Application for transfer from Associate Member.*)

MIDDLETON, Charles Roger, General Manager, Shell Refining & Marketing Co., Ltd. (*J. A. Oriel ; W. W. Goulston.*)

RALPH, Noël Albert, Chemist, Horton Manufacturing Co., Ltd. (*H. Heymann ; F. J. S. Hall.*)

SKILLING, Norman L., Regional Manager, Lubricating Oil Pool. (*C. Chilvers ; C. E. Burnett.*) (*Application for transfer from Associate Member.*)

STREETON, Reginald Douglas, Chemist, Petroleum Board. (*C. Chilvers ; A. Hamilton.*) (*Application for transfer from Student.*)

WALTON, Norman Lorraine, Chief Draughtsman, Messrs. Moore & Charlton. (*H. Moore ; H. E. Charlton.*)

ARTHUR W. EASTLAKE,
Honorary Secretary.

ANNUAL REVIEWS OF PETROLEUM TECHNOLOGY

Vol. 5 (Covering 1939)

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Vol. 27. No. 211. May 1941.

THE EFFECT OF CROOKED WELLS ON EXPLOITATION.*

By H. C. H. Thomas, M.A., A.R.S.M.

The purpose of these notes is to direct attention to the adverse effects of crooked or unintentionally deviated wells on the orderly exploitation of an oil-field.

It is not within the scope of the paper to inquire into methods developed to avoid the drilling of crooked hole. The mechanical disadvantages which may occur during the drilling or producing life of the well are only referred to in so far as they may affect the efficiency of exploitation.

I. Classification of Non-Vertical Wells.

Non-vertical wells can be classified in two main groups:

A. Wells intentionally drilled with a deviation.
B. Wells unintentionally drilled with a deviation.

Group A represents a special technique, which is not dealt with here. Group B can be subdivided as follows:

1. Wells which are crooked, and penetrate the producing horizon in random positions.
2. Wells which, although crooked, deviate in one direction, and consequently are straight in a plane at right angles to the direction of deviation.
3. Wells which, although crooked, spiral so that they penetrate the producing horizon vertically below the surface location.
4. Wells which are straight, although not vertical.

The very great majority of wells fall in groups B 1 and B 2. Broadly speaking, wells in group B 1 are the result of limitations of drilling methods, whilst those in group B 2 have additionally been affected by lithology and structure. Those in B 3 are probably rare, although there is frequently a *tendency* to spiral. Such spiralling tendency may be entirely the result of the rotation of the drill-pipe, and under different conditions seems to appear as a left-handed or right-handed spiral. It may, on the other hand, be an effect of dip, for if the well, owing to mechanical causes, starts to deviate in a direction contrary to that which the dip would impose on it, it may swing left- or right-handed into the imposed direction, rather than change the direction in the plane of the original deviation.

Wells in group B 4 represent a particular variation of those in group B 2, and are probably confined to shallow wells.

At this point it may be well to stress that, without directional surveys,

* Paper presented to a Meeting of the Trinidad Branch of the Institute of Petroleum on 26th June, 1940.

it is usually impossible to decide in which sub-group any particular well falls. The possible exception is where underground structure as derived from well depths is obviously at variance with surface geology.

II. Causes of Crooked Hole.

Nearly all the contributory causes to the drilling of crooked hole can be classified under two broad heads, Drilling and Formation.

Drilling.

It is only necessary to see the sag in a stand of drill-pipe standing in the derrick to realize that a string of drill-pipe is, in effect, a hollow flexible shaft which transmits the power from the rotary table to the bit.

In order to overcome the limitations imposed by the flexible nature of the drill-pipe, heavy and rigid drill-collars of large diameter are used on the bottom of the drilling string.

Two effects are looked for: first, that the concentrated weight of drill-collars at the bottom of the string will give a plumb-bob effect; second, that the rigidity and large diameter of the drill-collars will compel the bit to continue in the direction in which it has been started.

When drilling is in progress some or all of the weight of the drill-collars, and perhaps some of the drill-pipe as well, rests on the bottom of the hole. This part of the drilling string is in compression, and will tend to bow, causing the bit to wander. By using a small amount of weight on the bit, we endeavour to make use of the plumb-bob effect, and avoid the bowing of the drill-collar stand.

If a well is not vertical to start with, the plumb-bob effect, if any, should tend to pull it to the vertical, the rigidity and large diameter of the drill-collars would tend to maintain any deviation with which the well is started, and the bowing effect would be to make it deviate further.

Our experience shows that the last effect is the most pronounced. In fact, the question of starting wells straight is of the utmost importance, more particularly if the maximum size of hole is to be drilled through the conductor. If a large conductor is set in a crooked hole, and only small hole is to be drilled below it, then, as the bit reaches the bottom of the large hole after drilling out the shoe, some plumb-bob effect can be expected.

Formation.

It was mentioned above that the carrying of the weight of the lower part of the drilling string on the bottom of the hole, as occurs when drilling, will cause a tendency to bow, and crooked hole will result. In a homogeneous formation the chances of the bit drifting in any direction are equal, subject to any cork-screwing tendency caused by the rotation of the drill-pipe, and it would seem that in any formation lying flat the same would apply. Even a formation with a pronounced dip, if homogeneous, should theoretically not affect the course of the bit. Such homogeneous formations are, however, not the rule, and the actual small changes in hardness or drillability, when they occur in a dipping formation, will certainly influence the path of the bit. The question is, in what direction?

First, it would seem that the bit will endeavour to orient itself either at right angles to the bedding planes or parallel to them. In other words, the wells in any given area would generally go either up-dip or down-dip, and eventually to an extent where the deviation of the hole from the vertical would be equal to the dip or to the complement of the dip.

Of the factors on which the course taken by the well would depend, two seem to be of primary importance:

1. Value of dip.
2. Relative hardness of succeeding layers of formation.

1. *Value of Dip.*

From survey results in some Trinidad fields, it appears that when the dip is less than 35°, wells tend to drift up-dip. At greater values of dip they tend to drift down-dip or along strike. On the other hand, we have an insufficient number of surveyed wells in the latter category to generalize with safety. Moreover, except in certain areas, it would not be safe to assume that because the dip is less than the 35° every well which deviates does so in an up-dip direction. I quote here from a paper entitled "Problem of Crooked Holes" by F. H. Lahee: "If the rotating bit, which has been drilling in a soft formation, encounters a hard resistant layer, and if the beds have a moderate dip, the up-dip edge of the bit is checked, while the down-dip edge is still in soft material. If there is any play between the drill stem and the hole, as there generally is, this resistance tends to cause the stem to bend under weight and to bow down-dip, so that the bit is cutting more nearly perpendicular to the bedding. The bigger the hole is in relation to the size of the drill stem, the more opportunity would there be for this effect. On the contrary, if the strata dip steeply, such a hard layer would function like a wedge, forcing the bit to slide down its face while continuing to cut in the soft rock."

2. *Relative Hardness of Succeeding Layers of Formation.*

This is really an effect of dip coupled with the degree of homogeneity of the formation. As stated above, if the formation is completely homogeneous, the effect of dip will be nil. If frequent changes of formation of widely differing hardness occur, any effect of dip will be pronounced. Moreover, it seems probable that the hardness of the formation may influence the critical angle of dip, at which a well drifts up-dip or down-dip.

III. Results of Crooked Hole.

Some of the principal results of crooked holes are listed below, and amplified in succeeding paragraphs.

1. Incorrect spacing at the production level or levels, resulting in inefficient drainage.
2. Incorrect interpretation of structure.
3. Errors in forecasting.
4. Failure to complete the well.
5. Failure to produce the completed well to exhaustion.

Incorrect Spacing.

It is obvious that crooked hole adversely effects any methodic well-spacing, since, clearly, it is the spacing of the wells on the producing horizon(s) which is of primary importance. The producing horizon must be penetrated at selected regular intervals if it is to yield its greatest ultimate production. It is the usual assumption that a vertical well will be drilled, and appreciable expenditure is therefore incurred in placing the top of the well vertically over the point at which it is intended to pierce the producing horizon. Quoting from Lahee: "In the light of what we now know about the deviation of boreholes, the care with which well locations are measured off and surveyed on the ground becomes almost a joke."

Reference to Table II will show how seriously minor deviations can affect spacing at comparatively shallow depths.

TABLE I.

Table showing Extreme Distances between Two Adjacent Wells.

Depth.	Tolerance.	Surface spacing.			
		300	400	460	800
		Distance between two adjacent wells.			
1000	1°	Max.: 322 Min.: 278	422 378	482 438	822 778
2000	2°	Max.: 379 Min.: 221	479 321	539 381	879 721
3000	3°	Max.: 470 Min.: 130	570 230	630 290	970 630
4000	4°	Max.: 597 Min.: 3 *	697 103	757 163	1097 503
5000	5°	Max.: 759 Min.: −159 *	859 − 59 *	919 1 *	1259 341
6000	6°	Max.: 956 Min.: −356 *	1056 −256 *	1116 −196 *	1456 144

* Wells can meet or cross.

Table I assumes that deviation is consistently in one direction, and the figures given are for two wells which directly approach or directly depart from one another. This is treating the worst extremes, for it is obviously possible for all wells on a structure to drift in the same direction and to approximately the same extent. Further, it is possible that a crooked well may, by cork-screwing, penetrate the producing horizon vertically below its surface position.

Consider an ideal simple case of two wells, spaced on the surface, so that if straight hole is drilled and the wells are produced to exhaustion

the drainage areas will be circles the diameters of which are equal to the spacing between the wells—*e.g.*, 300 ft.

Then assume that while the one well is straight, the other well drifts

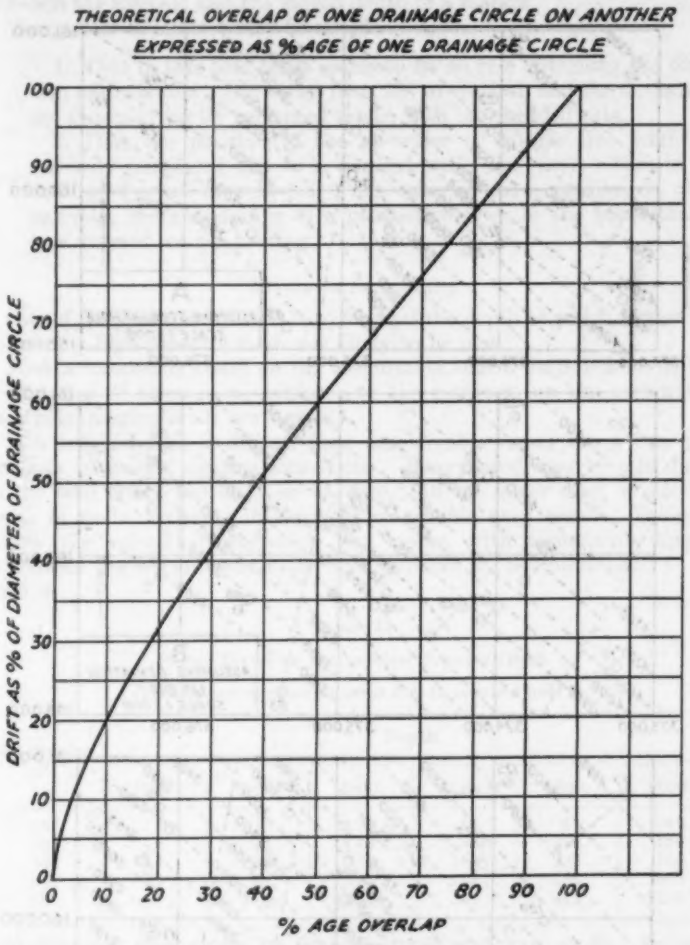


FIG. 1.

towards it. The chart (Fig. 1) shows the percentage overlap of the drainage areas, or the extra undrained area expressed as a percentage of the area theoretically drained by one well.

It is not proposed to enter here into the complex question of how such overlap will affect the ultimate extraction from the reservoir.

Incorrect Interpretation of Structure.

The effect of crooked hole on structural interpretation is illustrated by the three contour plans. It may be mentioned that these represent an actual case in a Trinidad field. Plan A (Fig. 2) is drawn on the assumption

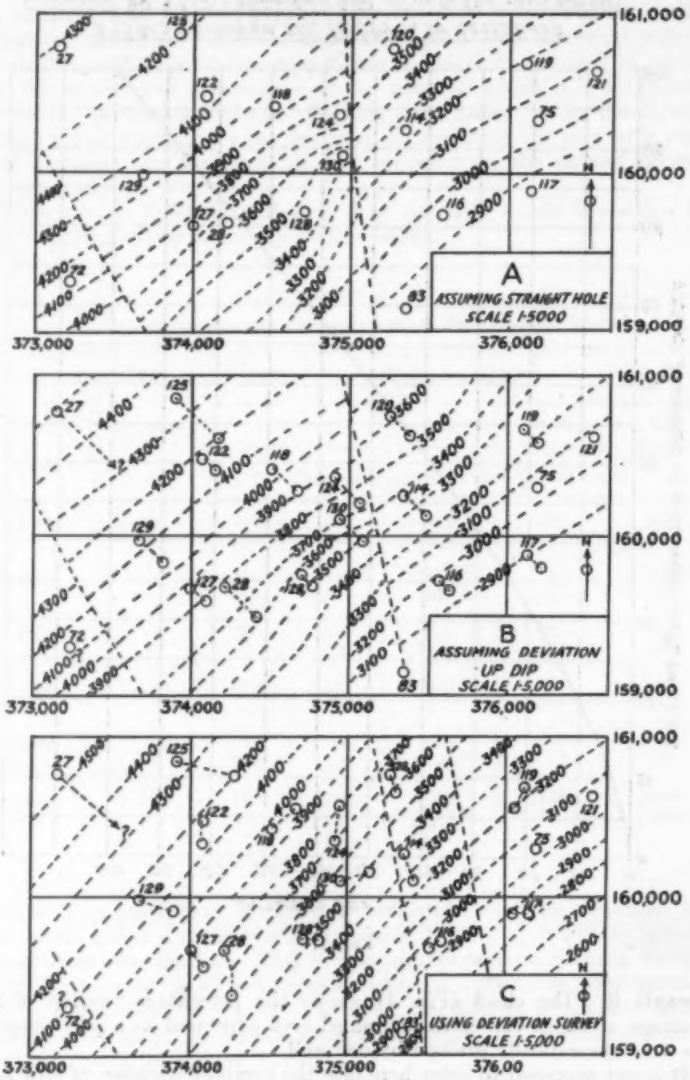


FIG. 2.

that the wells are straight. Plan B is based on the results of non-directional surveys, and it has been assumed that wells deviate up-dip. Plan C is based on directional surveys. In some recent wells in this area it has even been possible to estimate the deviation of the well from the difference between the forecast and the logged depth of a marker.

Two points of interest may be noted:

1. That in this field there seems to be no rule governing the direction of deviation. Dip varies from 35° to vertical, and the formations are generally partly cemented sands, with interbedded silts.

2. That the position of the oil–water or oil–gas line might be seriously misplaced due to a crooked well, and result either in the drilling of a well or wells below the water or above gas line, or, alternatively, the abandoning of a productive area, in the belief that it was watered, or gas-bearing.

Errors in Forecasting.

One of the geologist's duties is to forecast the depth at which formations containing high-pressure fluids are likely to be met.

Such a forecast is based on the assumption that a vertical hole will be drilled and, if there is no evidence to the contrary, on the assumption that neighbouring wells are vertical.

If a crooked hole is drilled, very considerable errors can occur, particularly in steeply dipping formations. Heavy mud may be introduced to the well either too early or too late. In the latter case, which will occur in wells deviating up-dip, serious trouble may result. Table II shows the minus errors which can occur with formations dipping at various angles, and where the hole deviates by not more than 1° per 1000 ft.

TABLE II.

Minus Errors in Feet against Forecast Depth.

(Table showing possible error due to crooked hole.)

Bed dipping at	Depth.					
	1000.	2000.	3000.	4000.	5000.	6000.
15°	3	10	23	40	61	88
30°	6	22	49	85	132	189
45°	11	39	85	148	229	328
60°	19	68	147	256	387	568
75°	41	145	317	553	854	1225

(*a*) Note that these figures are for wells deviating directly up-dip. For wells deviating down-dip errors are very considerably greater than those shown.

(*b*) Note that in a 4000-ft. well the deviation of which has increased steadily from 0° at surface to 4° at 4000 ft. a minus error of 85 ft. can occur in the forecast if the formation is dipping at 30°.

Failure to Complete the Well.

It is not intended to fully develop this aspect of crooked hole. Failure may result from mechanical breakdown, or simply because the well drifts

from productive into unproductive territory and cannot be brought back.

High power consumption, twist-offs, and stuck drill-pipe or casing are some of the more usual results of excessively crooked hole, and may result in the loss of the well.

An interesting case was reported recently in which, due to crooked hole, a rig was unable to reach its objective. This objective, a fault, was forecast at 6100 ft. At 4000 ft. the well had deviated 7°, and assuming no further deviation, the objective was re-forecast at 6750 ft., and this was beyond the capacity of the rig. (Note the 650 ft. of unnecessary drilling required.)

Failure to Produce the Completed Well to Exhaustion.

This may be due to collapse of the casing at a dog leg, or the loss of production equipment in the well due to excessive wear. Even if mechanical failure of the well does not occur, lifting the production from a crooked well may prove uneconomical in the later stages.

Thus it is seen that crooked hole affects every stage of exploitation. It may be mechanically impossible to drill straight holes in every type of formation, or the cost of doing so may be prohibitive. Nevertheless it is always possible to start a well straight, and to make some endeavour to keep it straight. A directional survey of every well drilled is not only of considerable value to the exploitation geologist, it is the only way in which we can assess the progress which is being made towards the drilling of straighter holes.

The author wishes to express his thanks to Messrs. Trinidad Leaseholds, Ltd., for their kind permission to present this paper, and to Messrs. Apex (Trinidad) Oilfields, Ltd., for the use of their club-house.

EXTREME-PRESSURE ADDITION AGENTS.*

By E. A. Evans and J. S. Elliott.

Byers (*National Petroleum News*, December 16th, 1936) gave a comprehensive list of patents relating to extreme-pressure lubricants. Van Voorhis brought the list up to date in a paper published in the *National Petroleum News*, March 6th, 1940. Both these publications must have been of the utmost value to those who are interested in extreme-pressure addition agents. The reader of these two articles might very well feel perplexed at the variety of materials patented, and the thoughts which drifted the chemist to those particular things. A little more light is shed upon the list if it is segregated, even roughly, into groups. Apart from a few miscellaneous materials, the additives may be classed generally as sulphur, chlorine, phosphorus, and nitrogen compounds. The sulphur compounds may be sub-divided into derivatives of mineral oils, fatty oils, organic acids, esters, polymers, and a variety of specific aliphatic and aromatic compounds. This simple classification does not lend itself quite so simply to the chlorine and phosphorus compounds.

It may be that the use of sulphur dates back to the time when flowers of sulphur were used in cutting oils. No one knew how it functioned, but the results were there. Logically, the sulphur dispersion was increased by the use of colloidal sulphur, and finally by sulphur in solution. Abrams, in U.S.P. 1,913,300, used dispersed particles intermediate in size between flowers of sulphur and the colloidal variety. He suspended free sulphur particles in oil by means of a mass of freely mobile gel particles of soap. Churchill disclosed in U.S.P. 1,974,299 (assigned to the Tidewater Oil Company) lubricants containing sulphurized fatty and mineral oils, and thereby advanced development a stage farther. U.S.P. 2,142,916 (Standard Oil Company, Ind.) introduced a refinement, by disclosing solvent-treatment of the sulphurized oil, presumably to remove the undesirable sulphur constituents which might be present.

When it had once been established that fatty oils could be sulphurized there was apparently little incentive to seek patent protection for the use of individual oils and fats; in any event, there are very few patents in this category. Cotton-seed and sperm oils have, however, been singled out for attention. The Gulf Research and Development Company has given consideration to the blending of sulphurized sperm oil with esters in conjunction with tricresyl phosphate (U.S.P. 2,179,067).

Exactly what happens when sulphur is heated with fatty oils is difficult to forecast, but when the sulphurizing is done with sulphur chlorides it is almost a hopeless task to sort out the reactions. It was surprising, therefore, that so much time was allocated to sulphurizing oils and organic acids on a commercial scale. Doubtless flexible displacements have served a useful purpose, particularly when standardization was at a lower ebb than it is to-day. For the time being it may be that we can forget the

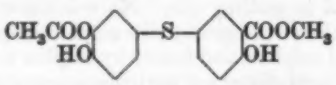
* Paper presented to a Meeting of the Institute in London, 5th February, 1941.

undefined compounds obtained from sulphurizing complex mixtures, and turn our attention to sulphur compounds of more exactly defined constitution. Before going over completely it should be borne in mind that there is an intermediate phase manifested in the sulphurized synthetic ester group. This group includes sulphurized esters of mono- and dihydric alcohols of somewhat complex composition; it also embraces the simpler type, of which sulphurized ethyl oleate is an example.

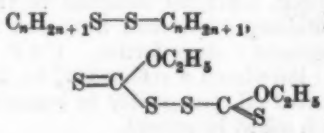
Contemporaneously with the developments above referred to, some attention was being given to the sulphurization of complex polymers which are obtained from cracking petroleum.

An early disclosure of the use of a pure organic compound occurs in U.S.P. 2,147,578, which relates to a simple sulphurized naphthalene. A later patent described the use of a sulphur compound of a dihydronaphthalene dimer.

Prior to these two patent publications one of us had been working on pure organic compounds, and had published the results in the General Discussion on Lubrication, I.M.E., 1937. It would appear, therefore, that this was the first, or at least one of the very early publications on the use of pure compounds for extreme-pressure lubrication. In this paper the film-rupture strength of a number of organic compounds was given, and special reference was made to di(3-carbomethoxy-4-hydroxyphenyl) thio-ether (B.P. 455,235).



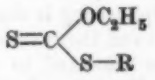
Shortly afterwards (in March 1938) U.S.P. 2,110,281 appeared, claiming the use of alkyl disulphides, aryl thiocyanates, and xanthic disulphides.



This patent, in the names of Adams and McNulty, was assigned to the Standard Oil Company, Ind.

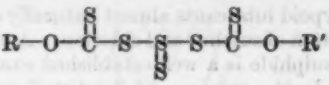
Sulphonic acid derivatives have not been an area for adventurous exploitation.

Thiocarbonates and allied compounds have been a source of considerable activity. U.S.P. 2,020,021, issued to the Standard Oil Company, Calif., relates to the simple thiocarbonates

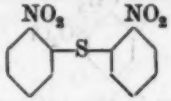


This thought has been extended to alkene trithiocarbonates (B.P. 488,483, N.V. de B.P.M.). Somewhat in the same family are the dialkyl xanthyl ethyl ethers (U.S.P. 2,161,584, Socony Vacuum). The use of xanthogen tetra-sulphides (B.P. 522,189) is of interest to us, and reference will be

made to this later in connection with our own researches on sulphur compounds.



Among the few types of additives containing both sulphur and nitrogen must be mentioned the aromatic compounds comprising divalent sulphur and nitro-groups, also mixtures comprising a divalent sulphur-containing component and a nitro group-containing component (B.P. 455,305). An example is a thioether containing two nitro groups:



Aliphatic nitriles R·CN, and thioamides, $R{\cdot}CSNH_2$, have been studied by Armour & Company.

The progress of the hypoid gear brought more and more into prominence mixtures of sulphurized oils and metal soaps. The principal characteristic of this type of lubricant is that it shall contain "corrosive" or "active" sulphur. Although several metal soaps have been suggested, a preference has always been exhibited for lead oleate or naphthenate.

Chlorine.

It is frequently believed that the halogenated compounds cannot maintain as high a load as the sulphur compounds. Whilst this belief is partly true, no such generalization is permissible.

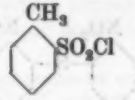
Concerning the hydrocarbons, there is an array of published patents sufficient to cover almost every type. B.P. 453,047 suggests that a minimum chlorine content of 55 per cent. is to be aimed at in all halogenated non-oxygenated organic compounds. This is emphasized by the fact that it succeeds B.P. 452,914 for halogenated non-volatile petroleum products, such as paraffin wax. This view, however, is not necessarily shared by other investigators, who have patented chlorinated diphenyl, aliphatic, and polyarylalkyl hydrocarbons.

Among oxygenated compounds, apart from sperm oil, carnauba wax, and other naturally occurring esters, interest has been confined to pure compounds. The range is wide, and extends from alcohols, ketones, esters, ethers to phenols. Specific application for use in diesel engines has been suggested for metallic salts of halogenated acids.

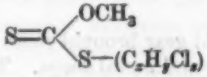
Halogenated condensation products may have been studied with internal-combustion engines in mind. Whatever the guiding thought may have been, the goal has been to synthesize a large molecule to combine E.P. properties with oiliness. Clearly, U.S.P. 1,939,995, which is concerned with the use of waxes condensed with halogenated fatty acids, discloses a step in this direction.

Sulphur and Chlorine.

The call for mild hypoid lubricants almost naturally drifted ideas towards a mixture or combination of sulphur and chlorine. A mixture of chlorinated wax and dibenzyl disulphide is a well-established example (B.P. 454,552). Other patents relate to the presence of "active" sulphur. Perhaps the simplest sulphur-chlorine compound which can be used is perchloromethyl mercaptan, $CSCl_4$. Owing to its character it can be used only under cold conditions. To extend its application Socony-Vacuum (U.S.P. 2,197,781) proposed to react it with unsaturated compounds. Another simple compound suggested is *o*-toluene sulphochloride (B.P. 449,311).

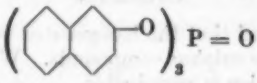


The thiocarbonates reappear in this category as chlorinated alkyl thiocarbonates (B.P. 519,288)

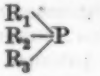


Phosphorus.

The long-known tricresyl phosphate may be regarded as the prototype of the phosphorus group, and tritolyl phosphate as a normal associate (B.P. 446,567). An allied compound is tri-β-naphthyl phosphate



The phosphates and phosphites so far prepared have insufficient E.P. properties to be used in gear oils. They have, however, been tried in I.C. engine oils. In this capacity tributyl phosphite has found favour in prolonging the life of cadmium bearings. Even phosphines

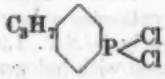


(R = aryl radicals)

have been suggested (U.S.P. 2,149,271).

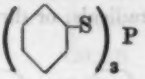
Phosphorus with Sulphur or Chlorine.

The simplest compounds in this group are the halogenated esters of phosphorus acids (B.P. 448,424). Alkylbenzene dichlorophosphines are also mentioned in U.S.P. 2,190,715.



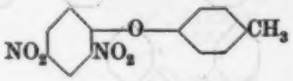
There are several patents for compounds containing both phosphorus

and sulphur, of which triaryltrithiophosphites (U.S.P. 2,188,943) are examples.



Nitrogen.

Whether nitrogen compounds have been put to practical use by themselves is unknown to us. That they might be useful is evidenced by patents granted to workers in different laboratories. Perhaps they have specific applications. Mention may be made of stearonitrile, $C_{17}H_{35}CN$ (U.S.P. 2,125,851), and alkyl phenyl oxy-ethers of 2 : 4-dinitrobenzene (U.S.P. 2,134,436).



Miscellaneous.

The list can be considerably extended by the inclusion of a variety of organic compounds. Experience may show that a number of them might be better classed as oiliness agents rather than E.P. agents. The division is often difficult, and the overlap extensive.

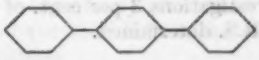
The compounds to which reference has been made have been selected as representatives in the classification. No marked thresholds divide the patent literature from our own line of attack. All that we claim in this paper is that we have endeavoured to classify other people's published work, and to augment the list of compounds from our own investigations.

Experimental.

As most of the hydrocarbons which might be used in any lubricant can be found within the range of mineral lubricating oils the film-rupture strengths of which lie between 3000 and 4000 lb. per sq. in., it is necessary to examine only a few. Since the Almen machine has been used for a number of years in our investigations on film strength, it is still used to obtain comparative data. Three representative hydrocarbons

Naphthalene

Diphenyl

Diphenylbenzene 

do not increase this strength, when dissolved in oil in concentrations of 1 per cent.

Bowden found that oleic acid reduced the coefficient of friction of mineral oils at low temperatures, but increased it at high temperatures. He found (B.P. 484,579) that a reduction of friction independent of temperature can be obtained by replacing the oleic acid with at least 1 per

cent. of organic compounds, consisting of at least three substituted and non-substituted rings which are interconnected, either indirectly, preferably by means of aliphatic radicals, or directly. Examples of such compounds are :—

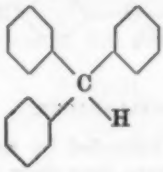
pp'-Dibenzyl diphenyl

Diphenyl benzidine

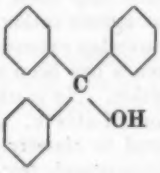
Dibenzylidene benzidine

Dibenzoyl benzidine

Triphenyl methane



Triphenyl carbinol



None of these affects the film-rupture strength (F.R.S.) when in 1 per cent. solution or suspension. Triphenyl carbinol is not readily soluble in mineral oil, consequently Bowden effected solution by using the mutual solvent methyl*cyclo*hexanol oxalate.

	F.R.S.
1% Triphenyl carbinol 2% Methyl*cyclo*hexanol oxalate 97% Oil	4,000
2% Triphenyl carbinol 4% Methyl*cyclo*hexanol oxalate 94% Oil	15,000

Esters.

In these investigations 3 per cent. of the ester was dissolved in mineral oil and the F.R.S. determined.

		F.R.S.
Amyl acetate	$CH_3 \cdot COOC_5H_{11}$	7,000
Butylene glycol diacetate	$CH_3 \cdot CH(COOCH_3) \cdot CH_2 \cdot CH_2 \cdot COOCH_3$	6,000
Amyl oxalate	$(COOC_5H_{11})_2$	5,000

		F.R.S.
Glyceryl oleate	$CH_2{\cdot}COOC_{17}H_{33}$ $CHOH$ CH_2OH	4,000
Benzyl oleate	$C_{17}H_{33}{\cdot}COOCH_2{\cdot}C_6H_5$	3,000
Ethyl benzoate	$C_6H_5{\cdot}COOC_2H_5$	8,000
Amyl benzoate	$C_6H_5{\cdot}COOC_5H_{11}$	8,000
Methyl salicylate		11,000
Diethyl phthalate		10,000
Butyl phthalate		5,000
Dibutyl phthalate		8,000

The wholly aliphatic esters gave low results. Similarly aliphatic acids when esterified with an aromatic alcohol gave low values. Aromatic acids, when linked with either low- or moderately high-molecular-weight aliphatic alcohols, gave somewhat higher results. The effect of very complex esters has not been studied from the point of view of film-rupture strength because of the difficulty in their preparation, and for the reason that they will probably be more useful as oiliness addition agents.

When the molecular weight of the alcoholic part in the molecule greatly exceeds that of the acidic part, or vice versa, the F.R.S. usually tends to be high, whereas a low F.R.S. is obtained when the molecular weights of the two parts of the molecule are of the same order.

The introduction of a nitro- or amino-group into an ester produces little effect, as illustrated by

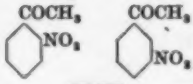
			F.R.S.
m-Nitroethyl benzoate		3%	8000
Ethyl anthranilate		1%	8000

The esters of phosphorus acids have been freely referred to in the patent literature. Most of them appear to have an F.R.S. in the range of 7000–10,000 when used in economic quantities.

Ketones.

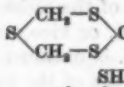
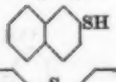
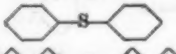
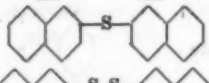
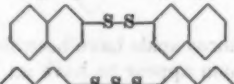
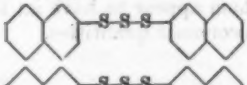
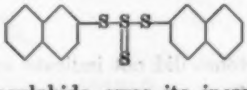
Simple aromatic ketones did not indicate sufficient promise to warrant extensive investigation.

A 1 per cent. solution in mineral oil of each ketone was used.

		F.R.S.
Acetophenone		4000
o- and *m*-Nitroacetophenone		7000
o-Aminoacetophenone		4000
m-Aminoacetophenone		4000

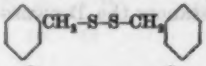
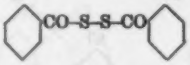
Sulphur.

Sulphur compounds offer an enormous and difficult field to survey. Whilst a preliminary search indicated promising avenues of approach, the considerable number of patented sulphur compounds clearly shows the need for a careful sifting of the groupings which build up the F.R.S. Even though thionyl chloride, $SOCl_2$, in as low a concentration as 0·1 per cent. in mineral oil gives a high F.R.S. it is unsuitable, because it is too volatile, and is very easily hydrolysed. It would seem from the following results that when sulphur is firmly held in a molecule, uninteresting results may be anticipated.

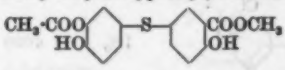
			F.R.S.
Carbon disulphide	CS_2	1%	2,000
Sulpho-ricinic acid	(from castor oil)	1%	5,000
Trithioformaldehyde		1%	4,000
α-Naphthyl mercaptan		1%	3,000
β-Naphthyl mercaptan		1%	4,000
Diphenyl sulphide		1%	6,000
β-Naphthyl sulphide		1%	4,000
β-Naphthyl disulphide		1%	5,000
β-Naphthyl trisulphide		1%	5,000
β-Naphthyl tetrasulphide		1%	10,000

No doubt β-naphthyl tetrasulphide owes its increased activity to the sulphur in the iso-position. A similar arrangement of four sulphur atoms

is found in the xanthogen tetrasulphides referred to earlier. The introduction of aliphatic carbon appears to render the sulphur more active.

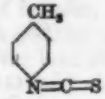
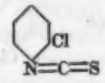
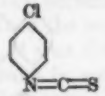
			F.R.S.
Dibenzyl disulphide		1%	8,000
" "		2·5%	15,000
Dibenzoyl disulphide		1%	9,000

Of the thioethers the examination of which has proved to be an interesting study, diphenyl sulphide is a simple example. Although of no value itself, it is the foundation of a valuable E.P. addition agent. Di-(3-carbomethoxy-4-hydroxyphenyl) thioether

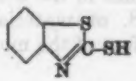
			F.R.S.
Di-(3-carbomethoxy-4-hydroxyphenyl) thioether		1%	15,000

illustrates how substituent groups can materially change the reactivity of a compound. Hydroxyl and carboxyl groups are of major importance in lubrication, yet it has still to be established whether they function independently of, or in conjunction with, the sulphur in this thioether.

Sulphur in a thiocarbimide might be expected to possess some activity, but such is not the case. It was not anticipated that the inclusion of one atom of chlorine would measurably increase the F.R.S. When the chlorine is placed in the *p*-position, however, a surprising result is attained.

			F.R.S.
p-Tolylthiocarbimide		5%	7,000
o-Chlorphenylthiocarbimide		5%	9,000
p-Chlorphenylthiocarbimide		5%	15,000

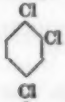
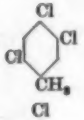
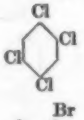
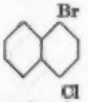
As mercaptobenzothiazole in very small concentrations has considerable utility in inhibiting corrosion, it is disappointing that it has no influence on film strength.

Mercaptobenzothiazole		1%	5000

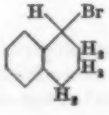
Chlorine.

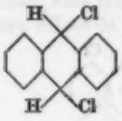
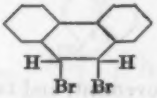
Whilst these investigations were in progress the maintenance of supplies of Almen pins and bushes became exceedingly difficult; therefore it was imperative that an alternative method of test should be found. Brownsdon (I.M.E. General Discussion on Lubrication, 1937) advocated wear im-

pressions as useful criteria in lubricant appraisals. He made no claim that wear impressions could be correlated with film strength, but in many instances the two take a parallel course. It was decided, therefore, that in the exceptional circumstances the Brownsdon machine could be used at least as a guide.

			F.R.S.	Wear.
Oil used			4000	0·415
Chlorbenzene		1%	—	0·430
p-Chlortoluene		2%	—	0·335
o-Dichlorbenzene		1%	4000	0·350
p-Dichlorbenzene		2%	4000	0·410
p-Dibromobenzene		1%	4000	—
2 : 4 : 5-Trichlortoluene		1%	9000	0·215
1 : 2 : 4 : 5-Tetrachlorbenzene		1%	6000	0·280
α-Bromonaphthalene		1%	4000	—
α-Chlornaphthalene		2%	4000	0·425

Less than three chlorine atoms in the benzene and the naphthalene nuclei do not improve the F.R.S. or materially affect the wear. Attention should be directed to the effect of the methyl group.

			F.R.S.	Wear.
5-Bromotetralin		1%	4,000	—
Tetrachlortetrahydro-naphthalene (mixture)		0·5% 1%	8,000 8,000	0·305 0·300

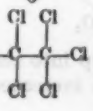
			F.R.S.	Wear.
Naphthalene tetrachloride		0·5% 1%	11,000 Over 15,000	0·230 0·230
Anthracene dichloride		0·5% 2% (suspension)	— —	0·285 0·150
Anthracene tetrachloride		1%	—	0·220
Phenanthrene dibromide		1% 2%	— —	0·350 0·250
Dichlorphenanthrene tetrachloride	Formula uncertain	2%	—	0·420

It is of interest to note that, as in the case of other substituents conferring E.P. properties, both the position of the halogen atoms in the nucleus and the manner in which they are present affect the improvement obtained.

In the foregoing group of compounds, the halogen is additively combined, except in the case of the chlorinated tetralin, and it is evident that such compounds merit special attention as addition agents. Thus, for example, naphthalene tetrachloride, which is the best of the compounds cited from a commercial viewpoint, is more beneficial than the mixture of isomers obtained by chlorinating "tetralin," although such a mixture may itself contain a minor amount of naphthalene tetrachloride.

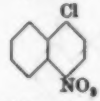
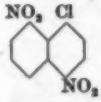
Dichlorphenanthrene tetrachloride presents a curious phenomenon. Although containing four added and two substituted chlorine atoms in the molecule, this substance does not reduce the wear. As it is scarcely likely that it will have a commercial value, it was not given specialized study.

As the aliphatic carbon is important in some sulphur compounds, it was considered advisable to test its influence on chlorine.

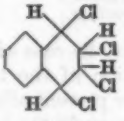
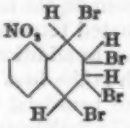
			F.R.S.	Wear.
Benzyl chloride		1%	7,000	0·265
Benzal chloride		1%	14,000	0·215
Hexachlorethane		1%	6,000	0·365

Benzyl chloride is thus superior to chlorobenzene, and benzal chloride to the dichlorbenzene. On the contrary, hexachlorethane does not compare favourably with 1 : 4-dichlornaphthalene tetrachloride, which also contains six chlorine atoms.

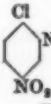
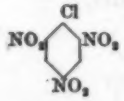
Nitro-chlor compounds.

			F.R.S.	Wear.
1-Chlor naphthalene		2%	—	0·425
1-Chlor-4-nitronaphthalene		2%	—	0·365
4 : 8-Dinitro-1-chlornaphthalene		2%	—	0·320

One nitro-group shows an improvement, and two augment it.

Naphthalene tetrachloride		1%	Over 15,000	0·230
α-Nitronaphthalene tetrabromide		1%	7,000	0·370

The tetrabromide was used because the nitro-tetrachloride is not known.

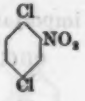
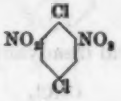
Chlorobenzene		1%	—	0·430
o-Nitro-chlorbenzene		1%	6,000	0·210
2 : 4-Dinitrochlorbenzene		1%	7,000	0·210
Picryl chloride		1%	—	0·330

The introduction of one nitro-group into the benzene nucleus produces an improvement which is somewhat increased by the introduction of a

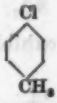
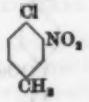
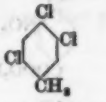
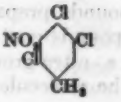
second; a third, however, results in a surprising loss of activity, a feature common to other compounds in which two nitro-groups are in the *o*-position to the same chlorine atom.

It should be noted that 2 : 4-dinitrochlorbenzene and certain other compounds containing two or more nitro-groups in conjunction with chlorine are powerful irritants, and unpleasant to handle.

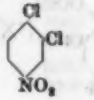
A similar extreme pressure effect is observed with *p*-dichlorbenzene.

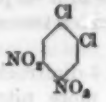
			F.R.S.	Wear
p-Dichlorbenzene		2%	4000	0·410
Nitro-*p*-dichlorbenzene		1%	7000	0·210
1 : 4-Dichlor-2 : 6-dinitrobenzene		1%	—	0·325

The introduction of an alkyl substituent has not a great effect.

p-Chlorotoluene		2%	—	0·335
3-Nitro-4-chlortoluene		1%	7000	0·230
		2%	—	0·210
2 : 4 : 5-Trichlortoluene		1%	9000	0·215
2 : 4 : 5-Trichlor-3-nitrotoluene		1%	9000	0·160

When the two nitro-groups are not symmetrically disposed about the chlorine then the cumulative effect is manifest.

o-Dichlorbenzene		1%	4000	0·350
1 : 2-Dichlor-4-nitrobenzene		1%	—	0·240

			F.R.S.	Wear.
1 : 2-Dichlor-4 : 5-dinitrobenzene		1%	—	0·210
1 : 2 : 4 : 5-Tetrachlorbenzene		1%	6000	0·280
1 : 2 : 4 : 5-Tetrachlor-3-nitro-benzene		1%	8000	0·240

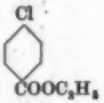
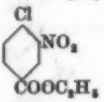
An aliphatic carbon atom is of importance.

			F.R.S.	Wear.
Benzal chloride		1%	14,000	0·215

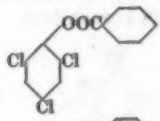
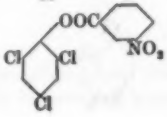
Benzal chloride has physiological disadvantages.

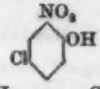
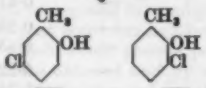
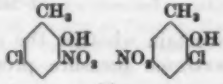
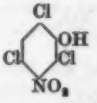
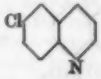
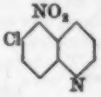
			F.R.S.	Wear.
p-Nitrobenzal chloride		1%	14,000	0·200

Amongst other compounds which exhibit the same phenomenon are

			F.R.S.	Wear.
Chlorinated ethyl benzoate		0·2%	—	0·390
Nitrochlor ethyl benzoate		0·2%	—	0 335

From the many nitro-compounds prepared it seems reasonably safe to assume that all aromatic compounds containing chlorine are improved in film-carrying capacity when a nitro-group is incorporated within the molecule, particularly when the molecule contains at least two halogen atoms.

			F.R.S.	Wear.
2 : 4 : 6-Trichlorphenyl benzoate		0·5%	—	0·330
2 : 4 : 6-Trichlor-phenyl-*m*-nitrobenzoate		0·5%	—	0·260

			F.R.S.	Wear.
2-Nitro-4-chlorphenol		1%	9000	0·235
Chlor-*o*-cresol		0·5%	—	0·250
Nitro-chlor-*o*-cresol		0·5%	8000	0·220
2 : 4 : 6-Trichlorphenol		0·5%	8000	0·260
2 : 4 : 6-Trichlor-3-nitrophenol		0·5%	9000	0·220
6-Chlorquinoline		2%	—	0·385
5-Nitro-6-chlorquinoline		2%	—	0·200

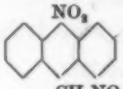
Mixtures.

So far the electronegative nitro-group has been studied only when it is in the same molecule as chlorine. Now it will be shown that the nitro-group can react when it is in a separate molecule from the chloro-compound, again with advantage accruing from the presence of at least two halogen atoms.

			F.R.S.	Wear.
2% Nitrobenzene	—	0·340	—	0·270
2% Chlorbenzene	—	0·410		
2% Nitrobenzene	5000	0·340	7000	0·280
1% *p*-Dichlorbenzene	4000	0·410		
1% *m*-Dinitrobenzene	5000	0·400	7000	0·285
1% *p*-Dichlorbenzene	4000	0·410		
2% *m*-Dinitrobenzene	—	0·400	—	0·170
1% Benzal chloride	—	0·215		
2% Nitrobenzene	5000	0·340	8000	0·210
1% Hexachlorethane	6000	0·365		
0·5% Naphthalene tetrachloride	—	0·230	—	0·230
1·0% α-Nitronaphthalene	—	0·420		
1% Hexachlorethane	6000	0·365	6000	0·355
1% α-Nitronaphthalene	4000	0·420		
2% *m*-Dinitrobenzene	5000	0·400	8000	0·210
2% Dichlordecahydronaphthalene	6000	0·230		
1% Nitrobenzene	5000	0·360	9000	0·210
0·5% 2 : 4 : 6-Trichlorphenol	8000	0·260		

			F.R.S.	Wear.
1% Tetranitromethane in *cyclo*hexanol	4000	0·370	4000	0·255
1% Chlorbenzene	4000	0·430		
1% Tetranitromethane in *cyclo*hexanol	—	0·370	—	0·265
1% *p*-Dichlorbenzene	—	0·410		
0·5% Nitroform	—	0·280	—	0·240
1·0% Chlorbenzene	—	0·430		
2% Phenylnitromethane	—	0·220	—	0·170
1% Hexachlorethane	—	0·365		

It now only remains to ascertain whether the nitro-group itself is the determining factor in the extreme pressure properties. The following examples show that it is not.

m-Dinitrobenzene		2% suspension	5000	0·400
α-Nitronaphthalene		1%	4000	—
9-Nitroanthracene		2% suspension	—	0·390
Phenylnitromethane		2%	—	0·220
Tetranitromethane	$C(NO_2)_4$	1% in 1% *cyclo*hexanol	4000	0·370
Nitroform	$HC(NO_2)_3$	0·5%	—	0·280
m-Nitro ethyl benzoate		1%	5000	0·410

In passing, it is interesting to note that the effect of an aliphatic carbon is also evident in a nitro-compound as shown in phenylnitromethane.

One may ask how many compounds having E.P. properties are being used commercially. It would be dangerous to hazard a guess, but it would be true to say that if many of them are being used, only a very small number have enjoyed extensive application. It may be that circumstances prejudice progress. Whatever obstacles there may be, the fact remains that film strength and film strengthening is a new phase of lubrication with a great future.

Our thanks are due to C. C. Wakefield & Co., Ltd., for permission to publish these results.

DISCUSSION

THE CHAIRMAN (DR. A. E. DUNSTAN) congratulated the authors on having produced a comprehensive and thoughtful account of a subject vastly important but empirical to a degree. For some time past emphasis had been laid on the need for some component, added or inherent, which would possess polarity, but on the other hand the refiner had gone to the opposite extreme and by modern processes had provided an almost non-reactive material. Hence the need for additives. In last September's meeting of the American Chemical Society at Detroit, Beeck, Givens, Smith, and Williams contributed a valuable paper on the mechanism of wear prevention by addition agents. They summarised their findings by remarking that their work revealed complex relationships between the chemical and physical aspects of boundary lubrication, but a differentiation could be made between chemical polishing agents and "wedging materials"—the latter effect being a function of surface activity. He (the Chairman) would appreciate the authors' views on this conclusion.

He had been particularly impressed by the careful attempts to give a quantitative significance to the problem. It seemed to him that there remained still to be accomplished the analysis of the numerical results perhaps on the lines indicated above.

COL. S. J. M. AULD said he would like to support the Chairman in his remarks regarding the significance of the presentation of a paper of this nature during the war. It indicated an intention to maintain our equilibrium in scientific as in other matters and was an appreciation of the need, now greater than ever, of pressing on with investigation and technical development. He would also like to record the personal pleasure he had experienced in listening to Mr. Evans' presentation of the paper involving, as it had, so much careful work.

Out of so much material it was not possible even lightly in discussion to consider more than one or two aspects of the subject. The first he would choose was in regard to the actual measurements recorded. The criticism might be levelled against the paper in general that the results were all in terms of one machine. It was well established that no two so-called E.P. machines gave identical results or placed all the substances used as addition agents in the same order of merit as regards their load-carrying capacity. This certainly applied to the Timken, S.A.E., Almen, Cornell, 4-Ball and other machines with which he was acquainted. The conclusion apt to be drawn in some quarters was, therefore, that none of them was any real use in measuring practical values, and that only field tests or tests involving the use of gears such as the 4-Square axle rigs or corresponding observations on cutting surfaces could be of value. Such views would overlook the fact that all laboratory test machines told something in regard to anti-weld or prevention of film rupture. It might be only in relation to their own construction and therefore limited for the purpose of drawing broad conclusions, but nevertheless some information was there. It would not necessarily follow that one could arrive at a complete answer by carrying out similar observations on all known test machines, nor would it be practicable to do so. Many who worked with such kinds of apparatus felt that their results had some relationship with practice in individual cases. A good instance of that was the unquestioned broad relationship between the load carried by leaded greases in the Timken machine and their ability to withstand pressures in the large roller bearings as used in steel mills. He personally had found considerable value in the use of the Falex (Cornell) machine as a means of guiding the choice of materials and giving some comparison of their practical value in regard both to back axle lubricants and cutting oils. He felt, therefore, that there was considerable value to be gained from observations made even on one single machine as long as the observations were under identical conditions. Such a conclusion then permitted Messrs. Evans and Elliott's results to be considered on a far broader basis than they otherwise could.

The second main point which he would like to mention was the fact that this is basically a chemical problem. Whatever the mechanism of the E.P. materials, it was quite clear even from the different behaviour of varying substances that chemical reactions were at the back of it.

As pointed out by the authors all materials fell within certain wide categories, and there seemed little doubt that the thermal stability of the compounds concerned

had some relationship to the conditions under which they became most helpful in promoting the load-carrying capacity of the oils in which they were incorporated. This being the case, it was interesting but immaterial to the discussion what was the *modus operandi*. Reaction might result in (1) the removal of asperities; (2) the successive defoliation of hard structured layers, or (3) the formation of loosely adherent cushions on which the bearing surfaces could ride. It did not follow in his opinion that because the value was some measure of chemical reactivity that the quantities involved would be large. The temporary surfaces produced might only be of molecular dimensions and yet by either of the first two methods prevent welding by ripping off more substantial layers of metal. This, in fact, seemed to take place. On some test pieces the wear was considerable. There did not seem necessarily, therefore, to be any relationship between wear and load-carrying capacity. The former might be a purely mechanical effect, whereas the latter, as he said, was chemical. The dimensional factors of the reactivity were apparently time and temperature. That was why E.P.'s differed so much in their behaviour as between the chief types—lead, sulphur, chlorine, and phosphorus.

It was a big thing that Mr. Evans and his colleagues were attempting in endeavouring to seek some more exact relationship between chemical constitution and extreme pressure characteristics. It might seem so difficult as to be impossible, but it was only by patient and exact working of this kind that one could hope to arrive at general conclusions. There were, of course, certain lines of thought which could come to mind. A good many years ago he had carried out some work on the constitution of the inorganic polysulphides and had shown that those of calcium, for example, consisted of a basic sulphide nucleus to which were attached a chain of sulphur atoms successively more loosely combined. Some similar composition, he felt, might possibly be an explanation of the different reactivity of organic sulphur compounds, and in this respect he drew attention to the β-naphthyl sulphides which the authors had described, and where the F.R.S. had gradually increased until the tetrasulphide gave very substantial figures. He would like to know whether if one took any of these synthetic compounds, particularly the tetrasulphide, it might be possible to attach some more sulphur as a side chain to the existing sulphur and thereby still further increase the film rupture strength.

One point which had occurred to him was that water or material splitting off water should have E.P. characteristics since there was thus open a series of reactions on metals over a range of temperatures. Had Mr. Evans noted anything of this kind?

Dr. E. R. Redgrove said that he had always supposed that the function of these addition agents was to impart to the metal faces in contact, a contaminating film which prevented welding taking place, but in view of some of the examples brought forward by the authors it would appear that he might have to alter or at least to modify his views.

It was very surprising that in some cases an excess of the active principle in the molecule of the addition agent resulted in decreased efficiency and he would like to ask the authors whether they could offer any explanation. Was it due to physical or chemical properties?

Dr. Dunstan had raised a very interesting point. It might be that an excess of the active principle had a solvent effect on the protective or contaminating film, in which case a reduction in the amount of additive compound might be beneficial. Had the authors investigated this possibility?

Mr. J. L. Taylor said: I should first of all like to ask the authors if they have investigated mixtures of sulphur and chlorine compounds, and if so what were the results of their investigations.

The second point I would like to make is regarding wear. If there is anything in the corrosion theory, it seems to me that if an additive is effective in E.P. properties then wear should be large, and I would expect it to be shown up on any wear-measuring machine. The fact that those additives investigated which showed promise gave results indicating reduction of wear in the Brownsdon machine, would seem to indicate that the corrosion theory is untenable.

I should like to ask if the authors have observed a material with good properties in raising the F.R.S. which also gives a higher rate of wear than the mineral oil itself.

In conclusion, I should like to add my congratulations to the authors to those that have been expressed by other speakers, on their imagination in the conception of the work, their industry in carrying it out, and their courage in presenting it at a time like the present.

Mr. C. H. Barton said: It has been shown by Givens, Beeck, and Williams at the Emeryville Laboratory of Shell Development Co. (*Annual Review of Petroleum Technology for* 1939, p. 298, also *Proc. Roy. Soc.*, December 1940) that certain organic compounds of phosphorus and arsenic when dissolved in lubricating oil form phosphides and arsenides with iron or steel bearings under running conditions. The low melting point compounds formed in this way on the surface assist the bearing to run in and reduce the rate of wear. When the bearing is coated with a chemically inactive metal such as gold, the phosphorus and arsenic compounds are ineffective.

Mr. N. E. F. Hitchcock said: The remarks of the Chairman relating to the mechanism of E.P. additives and his own suggestion that it may be due to liberation of the active element in the nascent form, has led to an interesting discussion. It has been pointed out that this theory would forecast increasing E.P. activity, with increased loading of the molecule with the active atom. The behaviour of dichlorphenanthrene tetrachloride is anomalous to this rule. Might not the explanation of this be due to the juxtaposition of the two equally active chlorine atoms which combine on liberation to form a molecule? In this case one would expect decreased activity corresponding to the relative reactivity of molecular and nascent chlorine.

Mr. J. Romney said: It is as well to emphasize the difficulty of drawing conclusions from work of this type. The authors concentrated on one machine, the Almen, but it is well known, and has, in fact, already been mentioned here, that different film strength testing machines can give quite different results on the same oil. Even the methods of recording results make it difficult to correlate tests on different machines. The Almen records pressures in pounds per square inch, while the Timken records an acutal load in pounds, applied to the lever of the machine. Although attempts have been made to convert Timken loadings to pressures in pounds per square inch, these are not successful because in the Timken test, in which a ring rotates in contact with a stationary block, the area of contact changes during the test, as a wider and wider scar is worn on the block.

The authors recognize these difficulties, and Mr. Elliott has replied to a questioner by pointing out that the authors had to confine themselves largely to one machine because of the work which would be involved in using more than one. It is certainly true that to carry the work to completion it would be necessary to test all the materials on all the available machines, to vary the test temperatures, and to use as test pieces all the metals with which the treated oils might come into contact in service, a very tall order.

However, Mr. Elliott points out that the use of one machine does, at least, give a broad basis for selection, allowing interest to be focussed on those materials giving high film rupture strengths and rejection of those which do not. Even this is risky, since it is very possible that compounds giving low results on the Almen might give quite high results on the other test machines.

The authors mention a very large number of patents taken out for various compounds, and it has always mystified me that so many people rush into patenting materials which are so difficult to find by analysis when present in small proportions in mineral oil. The degree of protection afforded to the patentees must be very small indeed. If it had been possible to obtain master patents covering the use of, say, sulphur compounds or chlorine compounds as extreme pressure additives, there would have been some point in it.

The hypoid gear has, as a previous speaker pointed out, been responsible for all this work on extreme pressure lubrication. The way in which engineers submit such problems to the oil industry with a justified confidence that a solution will be found is a compliment to the industry. I have often thought that it would be a good idea to return the compliment. One of these days I shall hand an engineer a sample of pure water. It is cheap and readily available in quantity, and it will be up to him

to design an engine which will work well with the water as a lubricant. But I think I'll wait until I have retired from the oil industry.

Mr. H. L. West said: With regard to the method of action of extreme pressure lubricants, the published work on this subject seemed to indicate that there is a definite reaction between the metals and the lubricant, so that what is suitable for one pair of metals is not necessarily the best for another pair. Thus with the so-called "active" (to copper) lubricants evidence of sulphides and sulphates has been obtained, and it is concluded that the oxygen which is always present must be taken into account. With the chlorinated lubricants ferric chloride had been found to be present, and, under certain conditions, even ferric oxide. Some work had also been done on the substituted phosphines, and arsines, which showed that the metalloids present definitely formed alloys with the metal surfaces. Most of this work is, however, of American origin, and so far has not been substantiated.

It seemed a pity that the authors had not carried out any work on the chlorinated aliphatic compounds, and thus make the picture more complete. It seemed surprising also that so much work had been done on aromatic compounds with the halogen attached to the nucleus and so little with it in the side chains. It is well known that, in the nuclear halogen compounds, the halogen atom is very firmly held and cannot be hydrolysed, except in exceptional cases, by caustic soda, whereas the halogen in the side chain behaves more as in an aliphatic compound and is readily hydrolysed by alkali. It would be interesting to see what happened with longer side chains, and with several side chains attached to the nucleus.

The action of a polar group, such as the nitro grouping, in activating the halogen is well known and usually decreases the further away from the halogen atom the group occurs; thus the *ortho* nitro compound would be expected to be more reactive than the *meta* or *para*. In the case of the 1:4-dichlor-2:6-dinitrobenzene it would appear that the two nitro groups are neutralizing one another, and it would be interesting to see the results of the 1:4-dichlor-2:5-dinitrobenzene, that is, with the nitro groups in the *ortho* position to each chlorine atom.

Mr. H. D. Mansion wrote: The writer agrees in general with Colonel Auld's remarks that care should be exercised against placing too much reliance in the film strengths given by any one of the various E.P. lubricant testing machines.

In a research on Durability of Gears the I.A.E. Research Department has tested a number of E.P. dopes (a very small number compared with those tested by the authors, it may be noted), under extreme load conditions as the lubricant for spur gears. Most of the dopes tested showed a film rupture strength of at least 15,000 lb./sq. in. on the authors' Almen machine, this being the limit of load available, and being about four times the value for the base oil. In the gear testing machine, however, where scuffing (viz., seizure of the tooth profiles above and below the pitch line), was taken as the criterion of failure, these same dopes gave failure loads ranging from 1·64 to 2·80 times that of the base oil. Another machine known to the writer indicated that a very great increase in load-carrying capacity could be obtained by the use of a certain mild dope. The gear machine, however, indicated only some 10 per cent. increase in load capacity.

Some of these anomalous results must be accounted for, as mentioned by one speaker, by the fact that, on some machines, only a small increase in Hertz stress is caused by quite a large increase in load, since the wear which occurs in the early part of the test serves to increase greatly the bearing area. This cannot be said of the Almen machine, but here perhaps one may criticize the inability to go to high enough loads for testing the more powerful dopes, and the uncertainty of the testing temperature when failure is reached.

Whilst it is desirable to test E.P. lubricants under something more approaching service conditions than is offered by most of the so-called E.P. testing machines, it must be understood that the involute gear, in whatever form, is recognized to be far from ideal as a test specimen, since, even by the most accurate gear grinding methods, the reproducibility of form falls far short of what can be achieved on any type of circular specimen. There is also, of course, the disadvantage of cost. On the subject of the actual dopes themselves, the writer, not being a chemist, will make no comment, but would like to express, in conclusion, his appreciation of the great service

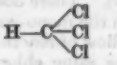
rendered by the authors in carrying out, and in publishing, their work on so extensive a range of addition agents.

PROF. A. W. NASH wrote: The authors are to be congratulated on the presentation of an important investigation. I have found the paper particularly interesting as very similar work was completed in my own Department about two years ago. Whereas the authors employed the Almen machine for their film strength determinations, our work was carried out with the Shell Four Ball machine. Another point of difference was the concentration of addition agent employed. We used 10 gms. of dope in 200 gms. of mineral oil compared with the 1–3 per cent. concentrations mentioned in the present paper.

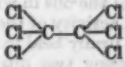
It is rather interesting to compare for identical compounds our results with those reported. For example, the authors rate aromatic chloro compounds in increasing efficiency as follows:—chlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene, benzyl chloride and benzal chloride. Our rating for these compounds is somewhat different, being in order of increasing efficiency—chlorobenzene, *o*-dichlorobenzene, benzyl chloride, *p*-dichlorobenzene and benzal chloride.

We have found *p*-dichlorobenzene to be more effective than *o*-dichlorobenzene, *p*-chlorophenol to be better than *o*-chlorophenol, and *p*-chloro-nitro benzene to be better than *o*-chloro-nitro benzene. Similarly the authors found *p*-chlorphenyl, thiocarbimide to be more effective than *o*-chlorophenylthiocarbimide.

It is difficult to see why the *para*-derivative should be more effective than the *ortho*-. A possible explanation was advanced by Mr. F. G. Howard, who has carried out much of the work on E.P. additives in this Department. He suggested that the "availability" of the active group present in the additive may be an important factor. Whereas *o*-dichlorbenzene has all its chlorine concentrated on one side of the benzene ring, *p*-dichlorobenzene has its chlorine divided equally on opposite sides of the ring. If a molecule of each compound was brought towards a metal surface, the probability of a contact between the metal and a chlorine atom would in the case of the *para*-compound be about twice that in the case of the *ortho*-form. In this respect the results obtained for chloroform and hexachlorethane were interesting. In both compounds the active component is chlorine and it will be seen from the formulæ:



Chloroform



Hexachlorethane

that in the case of hexachlorethane the possibility of a chlorine atom coming into contact with a metal surface is practically twice that in the case of chloroform. Thus the "availability" of chlorine in hexachlorethane is presumably twice that of chlorine in chloroform. As determined in the Four Ball machine hexachlorethane has a 2½ sec. seizure load of 126 kgs. as compared to a 2½ sec. seizure load of 98 kgs. for chloroform. That is, the hexachlorethane is about 1·3 times as effective as chloroform.

In the functioning of an additive many factors undoubtedly play an important part, such as high dipole moment, high chemical reactivity of the additive for metals, condensation of additive and oil to produce compounds chemically reactive to metals, etc. Nevertheless in certain instances the "availability" of the active group would appear to be of primary importance.

Author's Reply to the Discussion.

F. L. Miller of the Esso Laboratories, at the General Discussion on Lubrication, 1937, stated: "To measure load-carrying ability by actual gear or car tests is both tedious and costly, and is rarely feasible. Great impetus has thus been given to the development of simpler and more convenient test machines. Although all the machines purport to measure the same property of lubricants, hardly any two show even reasonable agreement as to the relative order in which they rate the load-carrying abilities of different types of lubricants." By his own showing the S.A.E. machine and the Almen classify the lubricants more or less in the same order, within the limits of the respective machines. It is generally accepted that no laboratory apparatus can take the place of the actual gear, but without laboratory methods, even incom-

plete ones, progress would be exceedingly slow and uneventful. The Almen machine may have limitations, but the charitable will regard it as an anchor in the deep sea of uncertainty. The only method available to satisfy a hopeful thought is to resort to a field test.

So far we have been fed on working hypotheses, to explain the mechanism of E.P. lubricants. There appears to be little experimental evidence to support the suggestion that a film of chloride or sulphide is formed. Finch, using electron diffraction methods, has shown that oxide films are produced, but at what stage they form he has not stated. This discovery is of considerable importance, particularly as we have shown that nitro and hydroxyl groups possess utility. A difficulty might be encountered in the case of phosphites which would ordinarily be regarded as reducing agents. Whether they could still be so regarded at 600° C. in close contact with bare metal under high pressure is open to speculation. Givens and his co-workers suggest that arsenic and phosphorus compounds function by combining with the metal surface, forming lower melting-point alloys. Students of surface phenomena will doubtless come to our aid to unravel the yet unknown reactions.

Even the congratulatory remarks of such deep thinkers as Dr. Dunstan and Col. Auld, which we greatly appreciate, will not draw us to express any opinion how E.P. lubricants perform their duties. We are diffident to accept the working hypotheses upon the scanty evidence, and we do not feel that our investigations go any further than to indicate that certain groups confer properties and certain others do not. "Wedging materials" might well be associated with polar groups and adsorption, but surely E.P. compounds should be inspected from the aspect of chemical activity, or as Col. Auld suggested, thermal stability.

The preparation of organic polysulphides was no easy matter, particularly the β-naphthyl tetrasulphide. Unfortunately the organic monosulphides cannot be induced to add sulphur as is the case with many inorganic sulphides.

Brownsdon showed that some interesting results could be obtained when water is added to wear-reducing agents. It is possible that di (3-carbomethoxy-4-hydroxyphenyl) thioether may split off water, but we do not know.

The contaminating film to which Dr. Redgrove has alluded is probably an oxide. The belief is borne out by the fact that the majority of E.P. compounds increase the rate of oxidation of the oils in which they are dissolved. There does, however, appear to be an optimum activity of the active principle. In the mono- and di-chlorbenzenes the chlorine is too firmly held to the benzene ring to allow of reaction, whereas in those compounds possessing two nitro-groups *ortho* to the same chlorine atom it would seem possible that the chlorine is lost so readily that only a portion of it can enter into reaction at the metal surface. The case of dichlorphenanthrene tetrachloride appears very exceptional. We have no explanation to offer.

Mr. Taylor will be pleased to know that we have considered mixtures of sulphur and chlorine compounds. We felt, however, that they were outside the scope of the paper. Although it might be true that an improvement does occur by their association, no generality can be assumed.

In an investigation of a wide range of compounds we have not found one which increases the wear when tested on the Brownsdon machine. This is not conclusive evidence that wear would not result in practice.

Messrs. Romney and Mansion will be glad to know that certain of our more promising compounds have been tested on the S.A.E. machine. Also we have made tests using the Almen machine at double its normal speed of rotation. The correlation has been reasonably satisfactory.

The work undertaken by Mr. Mansion at the I.A.E. Research Laboratory is very valuable. The investigations are being continued.

Professor Nash has raised exceedingly important points regarding "availability" of active groups. Except in the instance quoted of the chlorphenyl thiocarbimides we have not observed this effect. It will be noticed that *p*-dichlorbenzene in concentrations up to 2 per cent. has no apparent E.P. properties. It may be, however, that in concentrations as high as 5 per cent. other factors come into play. Perhaps the distribution of molecules of the addition agent and their orientation on the metal surface changes; availability then becomes important. All the results observed by Prof. Nash were obtained with concentrations of 5 per cent. In the only case when we used 5 per cent. we observed a similar effect. Most of our results were

obtained with concentrations of 3 per cent. and under. In none of these was the effect observed. From a commercial point of view 3 per cent. is more attractive!

The only excuse we can offer to Mr. West for not investigating the chlorinated aliphatic compounds is that they are referred to reasonably extensively in the patent literature. Probably after the war, when we have more time at our disposal, we shall be pleased to recall his suggestions.

There does not appear to be any direct evidence in the paper by Givens and his colleagues, in the Proceedings of the Royal Society, in support of the theoretical suggestion that chemical combination takes place between the metal surface and the phosphorus in the addition agent. It appears to us to be another working hypothesis. Finch has stated that whenever a compound containing sulphur, chlorine, or phosphorus has E.P. properties an amorphous oxide of metal is always formed on the metallic surface. We imagine this to be a very important discovery. It enables us to visualize the subsequent formation of a Beilby layer, which really carries the load. We are quite content to accept the disclosures of the electron camera, together with the idea of an amorphous oxide Beilby layer.

In conclusion we venture to suggest that workers on E.P. compounds might benefit by giving closer consideration to the Beilby layer.

EXTENSION OF THE OCTANE SCALE ABOVE 100 O.N.

REPORT AND RECOMMENDATIONS OF THE INSTITUTE OF PETROLEUM KNOCK-RATING OF AIRCRAFT FUELS PANEL.

(Approved by the Chemical Standardization Committee.)

Introduction.

As some experimental types of fuel have anti-knock values better than that of pure *iso*-octane, it has been considered desirable to provide an extension of the octane scale. The Sub-Committee of the above Panel recommended the following procedure, which has been approved, and is now recommended by the Chemical Standardization Committee.

Method of Test.

As no generally acceptable alternative to the A.S.T.M. Motor Method has been produced, it was decided to employ the Motor Method with such modifications as are necessary to obtain reliable ratings of high anti-knock value.

The method recommended is the Motor Method except that (*a*) the spark advance is fixed at 17° early, to reduce unsteady knocking which occurs above 100 O.N., and (*b*) the bouncing-pin lower-leaf spring-tension may have to be increased to prevent the pin from bouncing due to the higher combustion pressures. (Tensions up to 300 gms. have been found satisfactory.)

Scope of the Proposed "17° Motor Method".

The "17° Motor Method" is primarily intended for testing experimental types of fuel of over 100 O.N. (For the sake of continuity, experimental blends below 100 O.N. may also be tested by this method provided that they are reported suitably, *e.g.*, "98 O.N. 17° Motor Method'".)

Commercial Aviation fuels of nominally 100 O.N. should be tested as heretofore by Motor Method, even if the rating may be above 100 O.N.

Reference Fuels.

In order to obtain continuity of scale, it has been decided to employ the secondary reference fuels recommended by the Institute of Petroleum (*Journal*, February 1939, p. 106) from 92 O.N. up to 102 O.N.—namely, C + 4 mls. T.E.L./Imp. gln. and F + 4 mls. T.E.L./Imp. gln. In order that fresh batches of these secondaries may be calibrated from time to time, it is necessary to have a primary reference. This is achieved by using pure *iso*-octane + 4 mls. T.E.L./Imp. gln. and *n*-heptane + 4 mls. T.E.L./Imp. gln.

Scale.

The scale recommended extends from the O.N. of reference fuel C + 4 mls. T.E.L./Imp. gln. to that of F + 4 mls. T.E.L./Imp. gln. (C.12 + 4 mls./Imp. gln. = 93 O.N. approximately. F.3 + 4 mls./Imp. gln. = 116 O.N.)

Preparation of Primary Scale.

Blends of the leaded primary fuels were rated in terms of unleaded primary fuels up to 100 O.N. Above 100 O.N. the scale has been extrapolated and is recommended for adoption as the primary standard. This is presented in Fig. 1 and Table I.

The extrapolation is necessarily of an arbitrary nature, as the form of the calibration curve below 100 O.N. varies. The curve as presented will provide similar octane numbers to those given by the extrapolated secondary reference fuel calibrations referred to in the *Journal* for February 1939.

Table I.

Octane Number Calibration Tables for the Extension of the Octane Scale by the C.F.R. Motor Method (I.P.T. G.39 (T)) up to 100 O.N., thence by Extrapolation.

Iso-Octane + 4 mls. T.E.L./Imp. gln. in *n*-heptane + 4 mls. T.E.L./Imp. gln.

% Leaded Octane.	Octane No.	% Leaded Octane.	Octane No.
70	89·9	85	103·2
71	90·6	86	104·2
72	91·4	87	105·2
73	92·2	88	106·3
74	93·0	89	107·4
75	93·9	90	108·5
76	94·8	91	109·6
77	95·7	92	110·7
78	96·6	93	111·8
79	97·5	94	112·9
80	98·4	95	114·0
81	99·3	96	115·2
82	100·2	97	116·4
83	101·2	98	117·6
84	102·2	99	118·8
		100	120·0

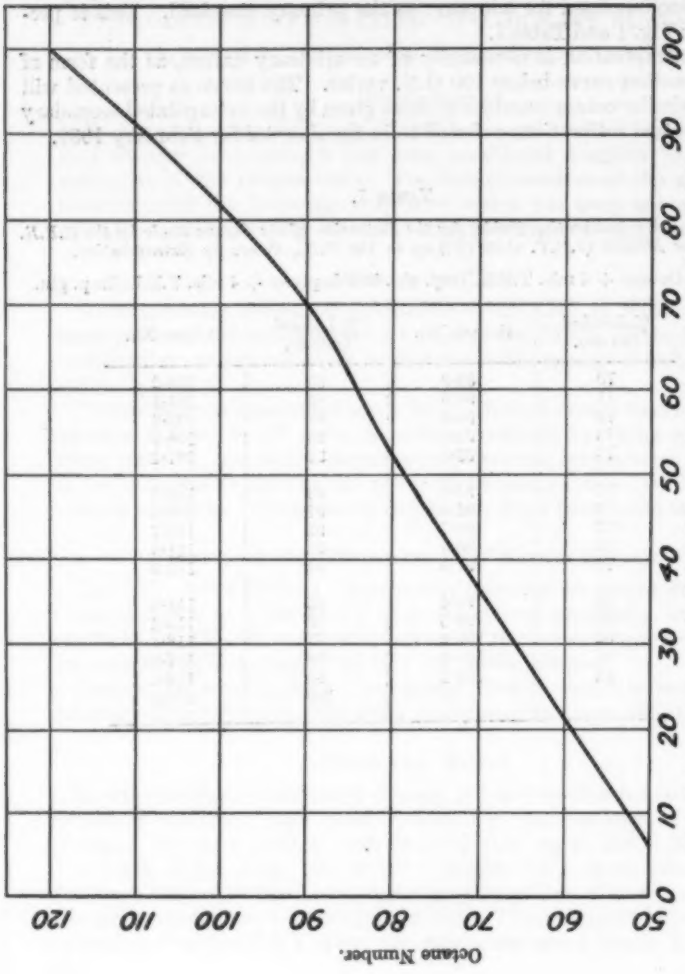


FIG. 1.

CALIBRATION (BY MOTOR METHOD) OF LEADED ISO-OCTANE AND N-HEPTANE AGAINST ISO-OCTANE AND N-HEPTANE.

TENTATIVE METHOD FOR KNOCK-RATING OF EXPERIMENTAL AVIATION FUELS OF OVER 100 O.N.

"17° MOTOR METHOD."

I.P.T. Serial Designation G.39b—1940 (T).

The apparatus and method shall be as laid down under Serial Designation G.39 (T) ("Standard Methods for Testing Petroleum and its Products," 3rd Edition, 1935, pp. 210–218), except that a fixed ignition setting of 17° early shall be used, and the bouncing-pin lower-leaf spring-tension increased to prevent the pin from bouncing as a result of higher combustion pressures. The spring tension may be increased if necessary for stable working up to a maximum of 300 grams.

The method is primarily intended for testing experimental types of fuel of over 100 O.N.

The primary scale is in terms of pure *iso*-octane and *n*-heptane up to 100 O.N., thence by extrapolation up to 120 O.N.

Leaded secondary reference fuels are calibrated in terms of leaded primary reference fuels which have been calibrated and approved from 90 O.N. to 120 O.N. (see Table I).

TABLE I.

Octane Number Calibration Tables for the Extension of the Octane Scale obtained by the C.F.R. Motor Method (I.P.T. G.39 (T)) up to 100 O.N., thence by Extrapolation.

% Leaded Octane.	Octane No.	% Leaded Octane.	Octane No.
70	89·9	85	103·2
71	90·6	86	104·2
72	91·4	87	105·2
73	92·2	88	106·3
74	93·0	89	107·4
75	93·9	90	108·5
76	94·8	91	109·6
77	95·7	92	110·7
78	96·6	93	111·8
79	97·5	94	112·9
80	98·4	95	114·0
81	99·3	96	115·2
82	100·2	97	116·4
83	101·2	98	117·6
84	102·2	99	118·8
		100	120·0

CALIBRATION OF C.F.R. REFERENCE FUELS.

Calibration of Secondary Reference Fuels F.3 + 4 Mls. T.E.L./Imp. Gln. and C.12 + 4 mls. T.E.L./Imp. Gln. by the C.F.R. Motor Method (I.P.T. G.39 (T) and I.P.T. G.39b (T)).

The calibration of the above reference fuels has been determined and continued up to 116 octane number in accordance with the procedure described in the preceding report. In order to do this, it was necessary to prepare a calibration for leaded secondary reference fuels in terms of leaded primary reference fuels (see Fig. 2). The final calibration (Fig. 3) is arrived at by interpolation from Figs. 1 and 2.

In order to conform with modern practice and to provide an accurate means of interpolating results, Fig. 3 is expressed below in tabular form.

TABLE II.

Octane-number Calibration Tables C.F.R. Motor Method (I.P.T. G.39 (T)) up to 100 O.N., thence by I.P.T. "17° Motor Method."

F.3 + 4 mls. T.E.L./Imp. gln. in C.12 + 4 mls. T.E.L./Imp. gln.

% F.3 + T.E.L.	O.N.	% F.3 + T.E.L.	O.N.
0	93·3	50	103·0
2	93·7	52	103·4
4	94·0	54	103·9
6	94·4	56	104·4
8	94·8	58	104·8
10	95·2	60	105·2
12	95·6	62	105·7
14	96·0	64	106·2
16	96·4	66	106·6
18	96·8	68	107·0
20	97·2	70	107·5
22	97·5	72	108·0
24	97·9	74	108·5
26	98·3	76	109·0
28	98·7	78	109·5
30	99·1	80	110·0
32	99·4	82	110·5
34	99·8	84	111·0
36	100·2	86	111·5
38	100·6	88	112·1
40	101·0	90	112·7
42	101·4	92	113·3
44	101·8	94	114·0
46	102·2	96	114·6
48	102·6	98	115·3
		100	116·0

FIG. 2.

CALIBRATION (BY 17° MOTOR METHOD) OF LEADED ISO-OCTANE AND N-HEPTANE AGAINST LEADED F3/C12.

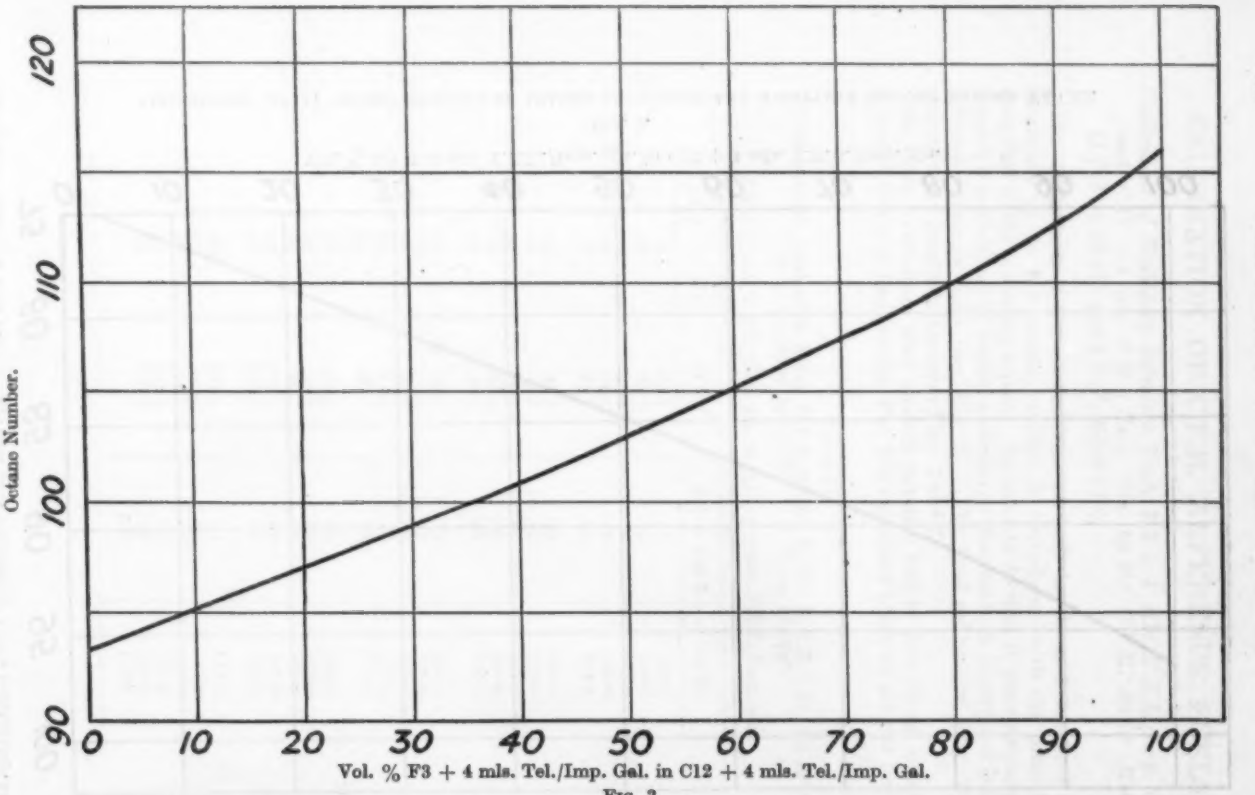


FIG. 3.

CALIBRATION CURVE. "C.F.R. MOTOR METHOD" UP TO 100 O.N. AND THENCE BY 17° MOTOR METHOD. (I.P.T. G. 39 (T).)

Approved by the Institute of Petroleum, London, March, 1941.

Blends of Standard Reference Fuels: F3 + 4 mls. Tetra-ethyl Lead per Imp. gln. and C12 + 4 mls. Tetra-ethyl Lead per Imp. gln.

CALIBRATION CURVE. "C.F.R. MOTOR METHOD" UP TO 100 O.N. AND THENCE BY 17° MOTOR METHOD. (I.P.T. G. 39 (T).)

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